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Work type : RES
Contract#: CTS-8915538 Mod #: AMENDMENT 6 Document : GRANT
Prime #: Contract entity: GTRC

Subprojects ? : N CFDA: 47.041
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Project unit: CHEM ENGR Unit code: 02.010.114
Project director(s):
WINNICK J CHEM ENGR (404)894-2839

Sponsor/division names: NATL SCIENCE FOUNDATION / GENERAL
Sponsor/division codes: 107 / 000

Award period: 900215 to 940131 (performance) 940430 (reports)

Sponsor amount	New this change	Total to date
Contract value	0.00	196,722.00
Funded	0.00	196,722.00
Cost sharing amount		9,823.00

Does subcontracting plan apply ?: N

Title: ELECTROCHEMICAL UTILIZATION OF HYDROGEN SULFIDE

PROJECT ADMINISTRATION DATA

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Security class (U,C,S,TS) : U ONR resident rep. is ACO (Y/N): N
Defense priority rating : N/A NSF supplemental sheet
Equipment title vests with: Sponsor GIT X

Administrative comments -
AMENDMENT 3 EXTENDS PROJECT TERM DATE THROUGH JANUARY 31, 1994. BUDGET REV. DTD 12-20-93 SHIFTS FUNDS BETWEEN BUDGET CATEGORIES.

GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION

NOTICE OF PROJECT CLOSEOUT

Closeout Notice Date 11/08/94

Project No. E-19-601 Center No. 10/24-6-R6900-0A0

Project Director WINNICK J School/Lab CHEM ENGR

Sponsor NATL SCIENCE FOUNDATION/GENERAL

Contract/Grant No. CTS-8915538 Contract Entity GTRC

Prime Contract No.

Title ELECTROCHEMICAL UTILIZATION OF HYDROGEN SULFIDE

Effective Completion Date 940131 (Performance) 940430 (Reports)

Closeout Actions Required:	Y/N	Date Submitted
Final Invoice or Copy of Final Invoice	N	
Final Report of Inventions and/or Subcontracts	N	
Government Property Inventory & Related Certificate	N	
Classified Material Certificate	N	
Release and Assignment	N	
Other	N	

Comments
LETTER OF CREDIT APPLIES. 98A SATISFIES PATENT REQUIREMENT.

Subproject Under Main Project No.

Continues Project No.

Distribution Required:

Project Director	Y
Administrative Network Representative	Y
GTRI Accounting/Grants and Contracts	Y
Procurement/Supply Services	Y
Research Property Managment	Y
Research Security Services	N
Reports Coordinator (OCA)	Y
GTRC	Y
Project File	Y
Other	N
	N

Electrochemical Utilization of Hydrogen Sulfide

Jack Winnick, Principal Investigator
School of Chemical Engineering
Georgia Institute of Technology

First Annual Report

February 14, 1991

National Science Foundation Grant No. CTS-8915538

Georgia Tech Account No. E-19-601

Summary

Because of its enormous supply and its chemical energy potential, H_2S has been targeted as a possible fuel for development in fuel cell research to be done in this laboratory. Past research has shown that even traces of H_2S are detrimental to molten carbonate fuel cells; however, studies suggest it as a strong possibility for use as a fuel in a solid oxide fuel cell. We will also pursue its use with proton conducting fuel cell systems.

The electrochemistry of this process is interesting; the products of the H_2S reaction in the solid oxide fuel cell include H_2O, SO_2, and S_2. However, the reactions actually occuring are unclear. The most desirable at the anode is:

$$H_2S + O^{2-} \Longrightarrow H_2O + 1/2\ S_2 + 2e^- \quad (1)$$

The least desirable is:

$$H_2S + 3O^{2-} \Longrightarrow H_2O + SO_2 + 2e^- \quad (2)$$

Thermodynamic and kinetic experiments are underway to determine the domain of each reaction. Further, the effect of catalyst on the reaction distribution will be examined.

The proton conducting fuel cell may provide a significant step in the conversion of H_2S to steam and elemental sulfur, because the half cell reactions are such that oxide ion and H_2S or sulfur are never in contact with each other. Thus, SO_2 will not be produced. Experiments similar to those for the oxide cell will be carried out in order to determine the thermodynamic and kinetic parameters.

Introduction

In the 1990's, over ten million tons of sulfur will be recovered annually from oil and gas sweetening processes in the United States. The sulfur is recovered from hydrogen sulfide, which is concentrated by any of several scrubbing/regeneration schemes. The energy available in this conversion

$$H_2S + 1/2\ O_2 \Longrightarrow S + H_2O \qquad (3)$$

is over 36 kcal/g mol. However, the Claus process, the overwhelming choice for conversion, discharges all of this energy as heat, captured mainly in the form of steam.

This same reaction, equation (3), if utilized through a fuel cell, with air as oxidant, would yield, at 900° C, an equilibrium potential of 0.79 volts. If a fuel cell stack can be operated at 80%, a realistic goal for high temperature operation, the 20% loss to heat is sufficient to maintain the stack and preheat the gases. In one scheme, In one scheme, a preheater would be used to bring the reactive gases to about 400°C. A regenerative heat exchanger would then bring the gases to cell temperature; the exhaust gases would leave the preheater at about 500°C, and then be used to generate steam from further power generation. At the projected rate of sulfur recovery, this amounts to a potential for over 1100 MW.

This potential has been obvious for decades; however, the means for its implementation has been elusive. A fuel cell requires electrodes for both fuel and oxidant; these must be good electronic conductors and be catalytic for the respective half cell reactions, undergoing no net chemical change. Between the electrodes, the

electrolyte system must be an ionic conductor (oxide or proton conductors), transporting negatively or positively charged ions at a rate equivalent to the current density. Both types of electrolyte systems will be studied in the course of this work.

Development of H_2S Fuel Cells

Electrolyte stability has been a major hindrance in H_2S fuel cell development. With an acidic electrolyte, the anodic oxidation of H_2S is as follows:

$$H_2S \Longrightarrow 2H^+ + S + 2e^- \quad (4)$$

However, liquid and solid sulfur are powerful insulators and will cause deactivation of the electrode. With a basic electrolyte, the reaction is as follows:

$$H_2S + 2OH^- \Longrightarrow 2H_2O + S + 2e^- \quad (5)$$

In this case, the sulfur dissolves to form sulfides and polysulfides.

Higher temperature phosphoric acid fuel cells and molten carbonate fuel cells have been shown to operate successfully with only ppm levels of H_2S; the electrolytes are unfavorably altered by H_2S during operation. However, solid oxide fuel cells have been found to be tolerant of high levels of H_2S.

Research Goals

Fuel cell systems have been the focus of much research. For H_2/O_2 fuel cells, oxide conducting solid electrolyte systems have been developed from ZrO_2 and CeO_2. Similarly, proton conducting ceramic solid electrolyte systems have been developed based on $BaCeO_3$ and $SrCeO_3$. The H_2S/O_2 fuel cell utilizes H_2S as the fuel, and

II. Proton Conducting Electrolyte Systems

The recent development of proton conducting electrolyte systems provides an exciting possibility for use in the electrochemical utilization of hydrogen sulfide. At the time of the initial research proposal, the study of the H_2S fuel cell was limited to oxide conducting electrolyte systems. We have since expanded this study to include the development of similar proton conducting electrolyte systems. Proton conducting electrolytes have previously been successfully used in H_2 / O_2 fuel cells systems (4,5,6,7). The attractiveness of their application to the H_2S fuel cell is the elimination of SO_2 as a possible product. The half cell reactions are:

$$\text{Anode: } H_2S \Longrightarrow 2H^+ + 2e^- + 1/2\ S_2 \qquad (9)$$

$$\text{Cathode: } 1/2\ O_2 + 2H^+ + 2e^- \Longrightarrow H_2O \qquad (10)$$

Since oxides and electrons are not conducted across the electrolyte the sulfur species and oxides are never in direct contact; thus only water and sulfur are the possible products, and no SO_2 is produced.

Experimental

The ZrO_2 electrolyte is available commercially stabilized with Y_2O_3. Both CeO_2 and ZrO_2 electrolyte disks will be prepared on site as well. The procedure consists of mixing either CeO_2 or ZrO_2 powder with polyvinyl butyral and MEK. This slurry is used in a tape casting procedure and then air dried. The disks are then sintered at 1000° C in a furnace. The proton conducting electrolytes are prepared similarly

produces elemental sulfur and electrical energy. Two classes of fuel cells will be studied: one which has oxide conducting electrolyte and the other which has proton conducting electrolyte. The development of proton conducting electrolytes is exciting, because of its potential application to use in H_2S fuel cells, which we will study here.

I. Oxide Conducting Electrolyte Systems

The H_2S fuel cell with oxide conducting ZrO_2 electrolyte has previously been studied (1,2,3). We are examining the analogous cell using CeO_2 as the solid electrolyte. This electrolyte system is attractive because the higher conductivity of CeO_2 versus ZrO_2 allows the cell to be operated at a lower temperature (600° C instead of 1000° C). At present, the anodic reaction mechanisms are not fully known. The oxide conducting electrolyte half cell reactions may be as follows:

$$\text{Anode:} \quad H_2S + 3O^{2-} \Longrightarrow H_2O + SO_2 + 6e^- \tag{6}$$

$$H_2S + O^{2-} \Longrightarrow H_2O + 1/2\ S_2 + 2e^- \tag{7}$$

$$\text{Cathode:} \quad 1/2\ O_2 + 2e^- \Longrightarrow O^{2-} \tag{8}$$

Thus all three species (S_2, SO_2, and H_2O) are possible products.

TEMPERATURE	$E_{6,8}$ (Volts)	$E_{7,8}$ (Volts)
600° C	0.815 V	0.796 V
800° C	0.788 V	0.791 V
1000° C	0.761 V	0.785 V

by mixing CeO_2, $SrCO_3$, and Nd_2O_3 or mixing CeO_2, $BaCO_3$, and Yb_2O_3 and tape casting by the above mentioned procedure to prepare the solid electrolyte disks. Electrolyte systems are summarized in Table II.

In the initial experiments, platinum catalyst electrodes will be painted onto the electrolyte surface for both the anode and the cathode, as well as the reference electrode. In the later experiments, ceramics based on $La_xSr_{1-x}MnO_3$, as well as other perovskite electrodes will be tested. The ceramic electrocatalysts $La_{0.9}Sr_{0.1}MnO_3$ (cathode) and $LaMg_{0.05}Cr_{0.95}O_3$ (anode) have been manufactured and utilized in this laboratory for research in molten salt cells. In initial experiments in which these electrocatlaysts are used, they will be applied to the electrolyte as a thin paste. If these runs indicate further investigation, more efficient depositions will be tested. Later, other perovskite electrocatalysts will be tested. The ability to use these less expensive ceramic electrocatalysts will increase the economic feasibility of the cells for larger scale operation.

The cell housings will be made of silica sealed with alumina. High density ceramic tubes will be used for gas inlet and exits (see Figure 1). The housing apparatus will be held in a 1000 C furnace by a mechanical vise. The cell will be sealed on the electrolyte disk by glass O-rings.

Platinum wire will be used as the current carrier. Current collectors, also made of platinum, will be painted onto the electrolyte surface and be connected to the current carrier wire, which will lead out of the cell via the ceramic gas tubes.

Cyclic voltammetry will identify the electrical potentials at which the electrode

reactions occur. A potentiostat will measure the current drawn in the cell at these potentials. Inlet gas compositions will be monitored using gas chromatograph analysis. Product gas compositions will be similarly studied, monitoring the SO_2 production with thermal conductivity and flame photometric detection, which is precise to ppm measurements (see Figure 2). Similarly, an ion chromatograph will be used to monitor the SO_2 production and the H_2S inlet and exit compositions, as total sulfur expressed through sulfate. Ion chromatography will also be used to monitor the electrolyte and electrodes for composition changes that may occur via sulfur deposits during cell operation.

Among the experimental goals of this study are the concentration dependence of SO_2 on current, applied overpotential, temperature, and electro-catalysts chosen. Both full cell and half cell experiments will be performed; these include steady state polarization, cyclic voltammetry, gas analysis, and cell power performance. In the experiments involving proton conducting electrolyte fuel cells, elemental sulfur will be isolated and collected.

Achievements

1. Procured raw materials and ceramic samples
2. Procured ion chromatograph
3. Designed furnace, flow scheme
4. Initiated proton conductor scheme (patent applied for)

Facilities

A one-thousand square foot laboratory is dedicated to electrochemical studies. Equipment includes several PAR Model 371 potentiostats and one model 273. There are a number of X-Y recorders as well as X-Time recorders. There are three storage analog oscilloscopes, and a digital oscilloscopewith IBM-compatible diskette file storage.

Two programmable Hewlett-Packard gas chromatographs, housed in the laboratory, are used solely for these studies. An optional flame photometric detector allows sulfur species measurement down to ppm levels. A Dionex DX-100 Ion Chromatograph will also be used in these studies.

A large hood, used in prior high temperature work with hydrogen sulfide will house the furnace. Controls used for gas flow monitoring, analysis, and electronics are mounted outside the hood at a lab bench.

Table 1. H_2S FUEL CELL HALF CELL REACTIONS

Half Cell Reactions	Anode	Cathode
Class 1: Oxide Conducting Electrolyte	$H_2S + O^{2-} \Rightarrow H_2O + 1/2\ S_2 + 2e^-$ $H_2S + 3O^{2-} \Rightarrow H_2O + SO_2 + 6e^-$	$1/2\ O_2 + 2e^- \Rightarrow O^{2-}$
Class 2: Proton Conducting Electrolyte	$H_2S \Rightarrow 2H^+ + 2e^- + 1/2\ S_2$	$1/2\ O_2 + 2H^+ + 2e^- \Rightarrow H_2O$

Table II. H_2S FUEL CELL MATERIALS

Products	**Prepared From**	**Preparation**	**Experimental Uses**
ZrO_2 (8 Y_2O_3)	ZrO_2, Y_2O_3, MEK, polyvinyl butyral	Commercially available and by solid state rxn on site, tape casting	Oxide Conducting Electrolyte
CeO_2 (8 Y_2O_3)	CeO_2, Y_2O_3, MEK, polyvinyl butyral	Solid state rxn on site, tape casting	Oxide Conducting Electrolyte
$BaCe_xNd_{1-x}O_{3-}$	$BaCO_3$, CeO_2, Nd_2O_3, MEK, polyvinyl butyral	Solid state rxn, tape casting	Proton Conducting Electrolyte

$SrCe_xYb_{1-x}O_{3-}$	$SrCO_3$, CeO_2, Yb_2O_3, MEK, polyvinyl butyral	Laboratory preparation	Proton Conducting Electrolyte
Platinum Paint	Platinum	Commercially Available	Electrocatalyst
$LaSr_{0.9}Mn_{0.1}O_3$ $LaMg_{0.05}Cr_{0.95}O_3$		Previously Prepared on site	Electrocatalysts

Table III. FUEL CELL CONFIGURATIONS

Anodic Gas	Anode	Electrolyte	Cathode	Cathodic Gas
Class 1: Oxide	**Conductors**			
H_2	Pt Perovskites $(Ln_{1-x}M_xM'O_3)$ Ln=lanthanoid metal M=alkaline earth M'=trans. metal	ZrO_2 (8 Y_2O_3)	Pt Perovskites $(Ln_{1-x}M_xM'O_3)$ Ln=lanthanoid metal M=alkaline earth M'=trans. metal	O_2 (air)

Anodic Gas	Anode	Electrolyte	Cathode	Cathodic Gas
H_2S	Pt Perovskites?	ZrO_2 (8 Y_2O_3)	Pt Perovskites?	O_2 (air)
H_2	Pt Perovskites?	CeO_2-Y_2O_3	Pt $La_{0.6}Sr_{0.4}CoO_3$	O_2 (air)
* H_2S *	Pt	CeO_2-Y_2O_3 ?	Pt $La_xSr_{1-x}CoO_{3-}$?	O_2 (air)

Anodic Gas	Anode	Electrolyte	Cathode	Cathodic Gas
Class 2: Proton	**Conductors**			
H_2	Pt Perovskites	Proton Conductors $SrCe_{0.95}Yb_{0.05}O_3$ $SrCe_{0.9}Sc_{0.1}O_{3-}$ $BaCe_{0.9}Nd_{0.1}O_{3-}$	Pt Perovskites	O_2 (air)
* H_2S *	Pt Perovskites	New Area	Pt Perovskites	O_2 (air)

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2. Ong, B. G.; Lin, T. A.; and Mason, D.M. Abstract #531, Electrochem Soc. Meeting, May 1987.

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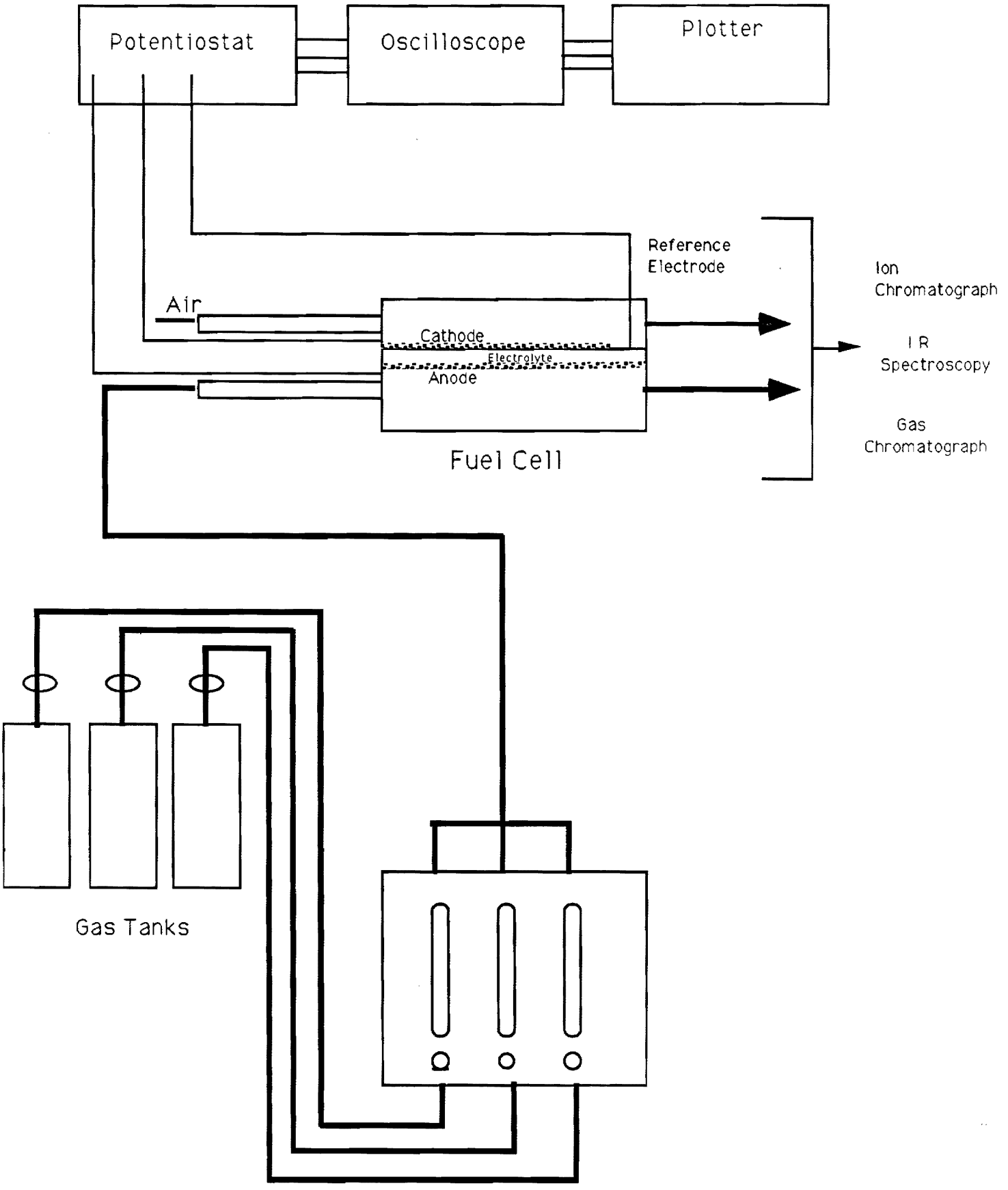
7. Iwahara, H., et al, J. Electrochem. Soc., 135, 529-533.

Experimental Set Up



Electrochemical Utilization of Hydrogen Sulfide

Jack Winnick, Principal Investigator
School of Chemical Engineering
Georgia Institute of Technology

Second Annual Report

March 1, 1992

National Science Foundation Grant No. CTS-8915538

Georgia Tech Account No. E-19-601

Summary

H_2S has been targeted as a possible fuel for development in fuel cell research to be done in this laboratory. The prospects are clear: H_2S is not only plentiful in supply, but, more importantly, it has much chemical energy potential. Detrimental to molten carbonate fuel cells even in trace amounts, H_2S has been suggested as a strong possibility for use as a fuel in a solid oxide fuel cell. We will also pursue its use with proton conducting fuel cell systems.

This process has interesting electrochemistry; the products of the H_2S reaction in the solid oxide fuel cell include H_2O, SO_2, and S_2. However, the actual reactions occurring and the selectivity are unclear. The most desirable reaction possible at the anode is:

$$H_2S + O^{2-} \Longrightarrow H_2O + 1/2\ S_2 + 2e^- \quad (1)$$

The least desirable is:

$$H_2S + 3O^{2-} \Longrightarrow H_2O + SO_2 + 2e^- \quad (2)$$

Thermodynamic and kinetic experiments are underway to determine the domain of each reaction. Further, the effect of catalyst on the reaction distribution will be examined.

A proton-conducting fuel cell may provide a significant step in the conversion of H_2S to steam and elemental sulfur, because the half cell reactions are such that oxide ion and H_2S or sulfur are never in contact with each other. Thus, SO_2 will not be produced. The individual half cell reactions are:

$$\text{Anode: } H_2S \Longrightarrow 2H^+ + 2e^- + 1/2\ S_2 \quad (3)$$

$$\text{Cathode: } 1/2\ O_2 + 2H^+ + 2e^- \Longrightarrow H_2O \quad (4)$$

Experiments similar to those for the oxide cell will be carried out in order to determine the thermodynamic and kinetic parameters.

Introduction

In the 1990's, over ten million tons of sulfur will be recovered annually from oil and gas sweetening processes in the United States. The sulfur is recovered from hydrogen sulfide, which is concentrated by any of several scrubbing/regeneration schemes. The energy available in this conversion

$$H_2S + 1/2\ O_2 \Longrightarrow S + H_2O \qquad (5)$$

is over 36 kcal/g mol. However, the Claus process, the overwhelming choice for conversion, discharges all of this energy as heat, captured mainly in the form of steam.

This same reaction, equation (3), if utilized through a fuel cell, with air as oxidant, would yield, at 900° C, an equilibrium potential of 0.79 volts. If a fuel cell stack can be operated at 80%, a realistic goal for high temperature operation, the 20% loss to heat is sufficient to maintain the stack and preheat the gases. In one scheme, In one scheme, a preheater would be used to bring the reactive gases to about 400°C. A regenerative heat exchanger would then bring the gases to cell temperature; the exhaust gases would leave the preheater at about 500°C, and then be used to generate steam from further power generation. At the projected rate of sulfur recovery, this amounts to a potential for over 1100 MW.

This potential has been obvious for decades; however, the means for its implementation has been elusive. A fuel cell requires electrodes for both fuel and

oxidant; these must be good electronic conductors and be catalytic for the respective half cell reactions, undergoing no net chemical change. Between the electrodes, the electrolyte system must be an ionic conductor (oxide or proton conductors), transporting negatively or positively charged ions at a rate equivalent to the current density. Both types of electrolyte systems will be studied in the course of this work.

Development of H_2S Fuel Cells

Electrolyte stability has been a major hindrance in H_2S fuel cell development. With an acidic electrolyte, the anodic oxidation of H_2S is as follows:

$$H_2S \Longrightarrow 2H^+ + S + 2e^- \quad (6)$$

However, liquid and solid sulfur are powerful insulators and will cause deactivation of the electrode. With a basic electrolyte, the reaction is as follows:

$$H_2S + 2OH^- \Longrightarrow 2H_2O + S + 2e^- \quad (7)$$

In this case, the sulfur dissolves to form sulfides and polysulfides.

Higher temperature phosphoric acid fuel cells and molten carbonate fuel cells have been shown to operate successfully with only ppm levels of H_2S; the electrolytes are unfavorably altered by H_2S during operation. However, solid oxide fuel cells have been found to be tolerant of high levels of H_2S.

State of Research

For H_2/O_2 fuel cells, oxide conducting solid electrolyte systems have been developed from ZrO_2 and CeO_2. Similarly, proton-conducting ceramic solid electrolyte systems have been developed based on $BaCeO_3$ and $SrCeO_3$. The H_2S/O_2 fuel cell

under current development in this laboratory utilizes H_2S as the fuel, and produces elemental sulfur and electrical energy. Two classes of fuel cells will be studied: one which has oxide-conducting electrolyte and the other which has proton-conducting electrolyte.

I. Oxide-Conducting Electrolyte Systems

The H_2S fuel cell with oxide conducting ZrO_2 electrolyte has previously been studied (1,2,3). We are examining the analogous cell using CeO_2 as the solid electrolyte. This electrolyte system is attractive because the higher conductivity of CeO_2 versus ZrO_2 allows the cell to be operated at a lower temperature (600° C instead of 1000° C). At present, the anodic reaction mechanisms are not fully known. The oxide conducting electrolyte half cell reactions may be as follows:

$$\text{Anode:} \quad H_2S + 3O^{2-} \Longrightarrow H_2O + SO_2 + 6e^- \tag{8}$$

$$H_2S + O^{2-} \Longrightarrow H_2O + 1/2\ S_2 + 2e^- \tag{9}$$

$$\text{Cathode:} \quad 1/2\ O_2 + 2e^- \Longrightarrow O^{2-} \tag{10}$$

Thus all three species (S_2, SO_2, and H_2O) are possible products.

TEMPERATURE	$E_{6,8}$ (Volts)	$E_{7,8}$ (Volts)
600° C	0.815 V	0.796 V
800° C	0.788 V	0.791 V
1000° C	0.761 V	0.785 V

Currently, electrolyte fabrication is the focus of the research effort. Two methods of manufacture are being examined: tape casting and uniaxial dry pressing.

The targeted electrolyte membrane thickness has been set at 1 mm. However, much thinner membranes are possible. By minimizing the electrolyte thickness, the subsequent IR drop is reduced, which consequently gives better cell performance. Tape casting is a method for membrane fabrication currently utilized by the microelectronics industry. The advantage that it offers is the ability to easily create very thin membranes.

The tape casting procedure consists of mixing the ceramic powders with a polymeric binder system in an organic solvent. This slurry is mixed in a jar mill and then poured onto a flat surface to be air dried. From this tape, disks are cut and then slowly heated through the temperature range in which the organic binder decomposes and "burns out." Once the binder is removed, the porous ceramic body left behind must be strengthened and densified. This is done by sintering, or heating the disk at temperatures near 1000° C in a furnace.

The problems frequently encountered in tape casting include binder burnout and warping or wrinkling. These problems are minimal in systems which require porous ceramic membranes, but are significant if dense membranes are required.

An alternative to tape casting is uniaxial dry pressing. Dry pressing is the better method when high density membranes are required. The process consists of mixing the ceramic powders with a binder and dispersant in a solvent, typically aqueous. The solvent is evaporated and the powders are pressed into "green body" disks. These disks are then sintered at temperatures up to 1600° C. Difficulties encountered in this method include binder burnout, uneven density, and warping.

II. Proton-Conducting Electrolyte Systems

The recent development of proton conducting electrolyte systems provides an exciting possibility for use in the electrochemical utilization of hydrogen sulfide. At the time of the initial research proposal, the study of the H_2S fuel cell was limited to oxide conducting electrolyte systems. We have since expanded this study to include the development of similar proton conducting electrolyte systems. Proton conducting electrolytes have previously been successfully used in H_2 / O_2 fuel cells systems (4,5,6,7). The attractiveness of their application to the H_2S fuel cell is the elimination of SO_2 as a possible product. The half cell reactions are:

$$\text{Anode:} \quad H_2S \Longrightarrow 2H^+ + 2e^- + 1/2\ S_2 \tag{11}$$

$$\text{Cathode:} \quad 1/2\ O_2 + 2H^+ + 2e^- \Longrightarrow H_2O \tag{12}$$

Since oxides and electrons are not conducted across the electrolyte the sulfur species and oxides are never in direct contact; thus only water and sulfur are the possible products, and no SO_2 is produced.

The fabrication of the proton-conducting membranes is similar to that of the oxide-conducting membranes. Both tape casting and uniaxial dry pressing techniques are appropriate and will be examined.

III. Experimental

A. Electrolyte Membrane

The primary step in membrane fabrication is the powder processing. In order to achieve a high (90+%) membrane density, the starting powder particle size should be small and have a narrow range. These two qualities allows for a more uniformly packed disk which sinters at a lower temperature and with less warping. A process

which yields oxide ceramic powders of these specifications is coprecipatation.

In this process, the metal nitrates of cerium and yttrium are first dissolved in de-ionized water. This solution is then added dropwise to an equivolume solution of ammonium hydroxide which is stirred. The resulting precipitate, an intimate chemical mixture of the hydroxides of the metals, is then filtered and given a series of washes. The first wash is with acetone, followed by a toluene wash, and finally another acetone wash. This oxide precipitate is then calcined at 450° C for two hours to yield the oxide mixture. The powders are then ground with a mortar and pestle and screened to less than 75 microns. The resulting oxides are then ready for membrane fabrication. Previous studies of the coprecipitation technique followed by the acetone, toluene, acetone wash have showed this method to yield powders of even less than 2 microns (8,9). The final powders have been characterized by X-ray crystallographic methods.

Electrolyte disks of CeO_2 are currently being prepared on site. A tape casting procedure has been studied using polyvinyl butyral binder and methyl ethyl ketone solvent. The tape cast disks have been manufactured by the procedure as mentioned earlier and then sintered at 1500° C in a furnace. Uniaxial pressing is also being investigated for membrane manufacture. Several binders are being used: polyvinyl alcohol (PVOH) (Kodak), methyl cellulose 4000 (Fischer Scientific), Methocel 20-122 (Dow), and polyvinyl butyral (Aldrich). The powders have been pressed at 20,000 psi and then sintered at 1500° C. Proton-conducting electrolytes will be manufactured similarly. Electrolyte systems are summarized in Table II.

B. Electrodes

In the initial experiments, platinum catalyst electrodes will be painted onto the electrolyte surface for both the anode and the cathode, as well as the reference electrode. In the later experiments, ceramics based on $La_xSr_{1-x}MnO_3$, as well as other perovskite electrodes will be tested. The ceramic electrocatalysts $La_{0.9}Sr_{0.1}MnO_3$ (cathode) and $LaMg_{0.05}Cr_{0.95}O_3$ (anode) have been manufactured and utilized in this laboratory for research in molten salt cells. In initial experiments in which these electrocatlaysts are used, they will be applied to the electrolyte as a thin paste. If these runs indicate further investigation, more efficient depositions will be tested. Later, other perovskite electrocatalysts will be tested. The ability to use these less expensive ceramic electrocatalysts will increase the economic feasibility of the cells for larger scale operation.

C. Cell Housings

The cell housings will be made of two different ceramics. First, housings made of silica sealed with alumina will be used. These housings are relatively porous, but are very stable at temperatures well above the operating range. Additionally, housings made of MACOR (Accuratus Ceramics) will be used. These housings are less porous and should provide better gas seals than the silica ones, but are limited in operating temperature. High density ceramic tubes will be used for gas inlet and exits (see Figure 1). The housing apparatus will be held in a 1000° C furnace by a mechanical vise. The cell will be sealed on the electrolyte disk by platinum O-rings.

Platinum wire (Englehard Corp) will be used as the current carrier. Current collectors, also made of platinum, will be painted onto the electrolyte surface and be connected to the current carrier wire, which will lead out of the cell via the ceramic

gas tubes.

D. Analytical Techniques

Cyclic voltammetry will identify the electrical potentials at which the electrode reactions occur. A potentiostat will measure the current drawn in the cell at these potentials. Inlet gas compositions will be monitored using gas chromatograph analysis. Product gas compositions will be similarly studied, monitoring the SO_2 production with thermal conductivity and flame photometric detection, which is precise to ppm measurements (see Figure 2). Similarly, an ion chromatograph will be used to monitor the SO_2 production and the H_2S inlet and exit compositions, as total sulfur expressed through sulfate. Ion chromatography will also be used to monitor the electrolyte and electrodes for composition changes that may occur via sulfur deposits during cell operation.

Among the experimental goals of this study are the concentration dependence of SO_2 on current, applied overpotential, temperature, and electrocatalysts chosen. Both full cell and half cell experiments will be performed; these include steady state polarization, cyclic voltammetry, gas analysis, and cell power performance. In the experiments involving proton conducting electrolyte fuel cells, elemental sulfur will be isolated and collected.

Recent Achievements

1. Constructed 1000° C furnace for cell experiments
2. Obtained and set up electrical components necessary for experiments

3. Tested operation of all components for cell experiments
4. Completed experimental set up in fume hood
5. Constructed multiple sets of cell housings from silica and macor
6. Developed coprecipitation and filtration washing process for fine particle size electrolyte powder preparation
7. Tested multiple binders for dry pressing electrolyte disks
8. Manufactured multiple "green body" electrolyte disks
9. Developed sintering process for electrolyte disks
10. Purchased current collector and carrier wires
11. Purchased initial electrode materials
12. Designed gas flow scheme
13. Initiated proton conductor scheme (patent applied for)
14. Obtained programmable 1700° C sintering furnace

Future Work

The current research emphasis is on electrolyte manufacture and initial cell runs. Multiple powder processing techniques will be further developed, the binder system will be developed, and sintering will be optimized. Initial full cell experiments with CeO_2 electrolyte and platinum electrodes will be performed.

Facilities

A one-thousand square foot laboratory is dedicated to electrochemical studies. Equipment includes several PAR Model 371 potentiostats and one model 273. There

are a number of X-Y recorders as well as X-Time recorders. There are three storage analog oscilloscopes, and a digital oscilloscope with IBM-compatible diskette file storage.

Two programmable Hewlett-Packard gas chromatographs, housed in the laboratory, are used solely for these studies. An optional flame photometric detector allows sulfur species measurement down to ppm levels. A Dionex DX-100 Ion Chromatograph will also be used in these studies.

A large hood, used in prior high temperature work with hydrogen sulfide will house the furnace. Controls used for gas flow monitoring, analysis, and electronics are mounted outside the hood at a lab bench.

Table 1. H_2S FUEL CELL HALF CELL REACTIONS

Half Cell Reactions	Anode	Cathode
Class 1: Oxide Conducting Electrolyte	$H_2S + O^{2-} \Rightarrow H_2O + 1/2\ S_2 + 2e^-$ $H_2S + 3O^{2-} \Rightarrow H_2O + SO_2 + 6e^-$	$1/2\ O_2 + 2e^- \Rightarrow O^{2-}$
Class 2: Proton Conducting Electrolyte	$H_2S \Rightarrow 2H^+ + 2e^- + 1/2\ S_2$	$1/2\ O_2 + 2H^+ + 2e^- \Rightarrow H_2O$

Table II. H_2S FUEL CELL MATERIALS

Products	**Prepared From**	**Preparation**	**Experimental Uses**
CeO_2 (8 Y_2O_3)	CeO_2, Y_2O_3, PVOH/Methocel Water	Uniaxial Dry Pressing (Already made)	Oxide Conducting Electrolyte
CeO_2 (8 Y_2O_3)	CeO_2, Y_2O_3, MEK, polyvinyl butyral	Solid state rxn on site, tape casting (Already made)	Oxide Conducting Electrolyte
$BaCe_xNd_{1-x}O_{3-}$	$BaCO_3$, CeO_2, Nd_2O_3, MEK, polyvinyl butyral	Solid state rxn, tape casting	Proton Conducting Electrolyte

$SrCe_xYb_{1-x}O_{3-}$	$SrCO_3$, CeO_2, Yb_2O_3, MEK, polyvinyl butyral	Laboratory preparation	Proton Conducting Electrolyte
Platinum Paint	Platinum	Commercially Available	Electrocatalyst
$LaSr_{0.9}Mn_{0.1}O_3$ $LaMg_{0.05}Cr_{0.95}O_3$		Previously Prepared on site	Electrocatalysts

Table III. FUEL CELL CONFIGURATIONS

Anodic Gas	Anode	Electrolyte	Cathode	Cathodic Gas
Class 1: Oxide	**Conductors**			
H_2	Pt Perovskites $(Ln_{1-x}M_xM'O_3)$ Ln=lanthanoid metal M=alkaline earth M'=trans. metal	ZrO_2 (8 Y_2O_3)	Pt Perovskites $(Ln_{1-x}M_xM'O_3)$ Ln=lanthanoid metal M=alkaline earth M'=trans. metal	O_2 (air)
H_2S	Pt Perovskites?	ZrO_2 (8 Y_2O_3)	Pt Perovskites?	O_2 (air)

Anodic Gas	Anode	Electrolyte	Cathode	Cathodic Gas
H_2	Pt Perovskites?	CeO_2-Y_2O_3	Pt $La_{0.6}Sr_{0.4}CoO_3$	O_2 (air)
* H_2S * (Research Target)	Pt	CeO_2-Y_2O_3 ?	Pt $La_xSr_{1-x}CoO_{3-}$?	O_2 (air)

Anodic Gas	Anode	Electrolyte	Cathode	Cathodic Gas
Class 2: Proton	**Conductors**			
H_2	Pt Perovskites	Proton Conductors $SrCe_{0.95}Yb_{0.05}O_3$ $SrCe_{0.9}Sc_{0.1}O_{3-}$ $BaCe_{0.9}Nd_{0.1}O_{3-}$	Pt Perovskites	O_2 (air)
* H_2S * (Research Target)	Pt Perovskites	New Area	Pt Perovskites	O_2 (air)

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NATIONAL SCIENCE FOUNDATION
FINAL PROJECT REPORT

PART I - PROJECT IDENTIFICATION INFORMATION

1. Program Official/Org. Maria Burka - CTS

2. Program Name CHEMICAL REACTION PROCESSES PROGRAM

3. Award Dates (MM/YY) From: 02/90 To: 07/93

4. Institution and Address

GA Tech Res Corp - GIT
Administration Building
Atlanta GA 30332

5. Award Number 8915538

6. Project Title

Electrochemical Utilization of Hydrogen Sulfide

This Packet Contains
NSF Form 98A
And 1 Return Envelope

: Grant Conditions (Article 17, GC-1, and Article 9, FDP-11) require submission of a Final Project ıort (NSF Form 98A) to the NSF program officer no later than 90 days alter the expiration of the ırd. Final Project Reports for expired awards must be received before new awards can be made F Grants Policy Manual Section 677).

w, or on a separate page attached to this form, provide a summary of the completed projects and technical information. Be to include your name and award number on each separate page. See below for more instructions.

PART II - SUMMARY OF COMPLETED PROJECT (for public use)

summary (about 200 words) must be self-contained and intelligible to a scientifically literate reader. Without restating the ɔct title, it should begin with a topic sentence stating the project's major thesis. The summary should include, if pertinent e project being described, the following items:

e primary objectives and scope of the project
e techniques or approaches used only to the degree necessary for comprehension
e findings and implications stated as concisely and informatively as possible

Attached

PART III - TECHNICAL INFORMATION (for program management use)

references to publications resulting from this award and briefly describe primary data, samples, physical collections, ıntions, software, etc. created or gathered in the course of the research and, if appropriate, how they are being made available ıe research community. Provide the NSF Invention Disclosure number for any invention.

Attached

tify to the best of my knowledge (1) the statements herein (excluding scientific hypotheses and scientific opinion) are true and complete, and ıe text and graphics in this report as well as any accompanying publications or other documents, unless otherwise indicated, are the original ‹ of the signatories or of individuals working under their supervision. I understand that willfully making a false statement or concealing a ərial fact in this report or any other communication submitted to NSF is a criminal offense (U.S. Code, Title 18, Section 1001).

	Aug 3, 1993
Principal Investigator/Project Director Signature	**Date**

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MAILING INSTRUCTIONS
Return this *entire* packet plus all attachments in the envelope attached to the back of this form. Please copy the information from Part I, Block I to the *Attention* block on the envelope.

NSF Project # 8915538

Electrochemical Utilization of Hydrogen Sulfide
Georgia Institute of Technology
Final Report

Part II Summary

A high-temperature fuel cell was sought, which would allow the direct conversion of hydrogen sulfide to sulfur and electrical energy, using air as the oxidant. Solid oxide electrolytes seem tolerant to hydrogen sulfide and operate at temperatures above the boiling point of sulfur, thus eliminating the poisoning effect of condensed sulfur at the negative electrode.

It was originally proposed to use oxide-conducting electrolytes with electrodes which promoted the partial oxidation to sulfur and water, and avoid the complete oxidation to sulfur dioxide. The latter would obviously be an emission problem. But in the course of the research it was found that some oxide electrolytes were, in fact, *proton* rather than oxide-ion conductors. Using these it is possible to directly de-protonate the hydrogen sulfide to sulfur at the negative electrode, eliminating the opportunity for sulfur dioxide production. The air oxidation at the positive electrode produces water vapor, which can safely be emitted.

Both the original and new scheme were tested in the laboratory. The highest power densities ever achieved with this type of fuel cell were reported. Effluent analysis shows that sulfur dioxide may be emitted with the standard cell design, but not with the new one. The work has pointed the way to electrode-electrolyte configurations which may be commercially viable.

NSF Project # 8915538

Electrochemical Utilization of Hydrogen Sulfide
Georgia Institute of Technology
Final Report

Part III Technical Information

T. Kirk and J. Winnick, "Hydrogen Sulfide/Air Solid Oxide Fuel Cell," *Proceedings of the 27th Intersociety Energy Conversion Engineering Conference*, 1992.

D. Peterson and J. Winnick, "A Ceria-Based Solid Oxide Fuel Cell," *Proceedings of the 28th Intersociety Energy Conversion Engineering Conference*, 1993.

T. Kirk and J. Winnick, "A Hydrogen Sulfide Solid Oxide Fuel Cell Using Ceria-Based Electrolytes," *Journal of the Electrochemical Society*, in press, 1993.

A new high-temperature solid oxide fuel cell was developed; it directly oxidizes hydrogen sulfide to elemental sulfur using air as the oxidant. This is possible because proton-conducting electrolytes have been substituted for the oxide-ion-conductors previously used.

Currents, voltages, and effluent analyses for all cell configurations are reported. Materials analysis techniques, such as x-ray diffraction and scanning electron microscopy, were used to characterize the solid-oxide electrolytes before and after use.

PART IV – FINAL PROJECT REPORT – SUMMARY DATA ON PROJECT PERSONNEL

(To be submitted to cognizant Program Officer upon completion of project)

The data requested below are important for the development of a statistical profile on the personnel supported by Federal grants. The information on this part is solicited in resonse to Public Law 99-383 and 42 USC 1885C. All information provided will be treated as confidential and will be safeguarded in accordance with the provisions of the Privacy Act of 1974. You should submit a single copy of this part with each final project report. However, submission of the requested information is not mandatory and is not a precondition of future award(s). Check the "Decline to Provide Information" box below if you do not wish to provide the nformation.

Please enter the numbers of individuals supported under this grant.
Do not enter information for individuals working less than 40 hours in any calendar year.

	Senior Staff		Post-Doctorals		Graduate Students		Under-Graduates		Other Participants[1]	
	Male	Fem.	Male	Fem.	Male	Fem.	Male	Fem.	Male	Fem.
A. Total, U.S. Citizens	1				2		1			
B. Total, Permanent Residents										
U.S. Citizens or Permanent Residents[2]:										
American Indian or Alaskan Native										
Asian.....										
Black, Not of Hispanic Origin.....										
Hispanic										
Pacific Islander										
White, Not of Hispanic Origin	1				2		1			
C. Total, Other Non-U.S. Citizens										
Specify Country 1.										
2.										
3.										
D. Total, All participants (A + B + C)	1				2		1			
Disabled[3]										

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[1] Category includes, for example, college and precollege teachers, conference and workshop participants.

[2] Use the category that best describes the ethnic/racial status to all U.S. Citizens and Non-citizens with Permanent Residency. *(If more than one category applies, use the one category that most closely reflects the person's recognition in the community.)*

[3] A person having a physical or mental impairment that substantially limits one or more major life activities; who has a record of such impairment; or who is regarded as having such impairment. *(Disabled individuals also should be counted under the appropriate ethnic/racial group unless they are classified as "Other Non-U.S. Citizens.")*

AMERICAN INDIAN OR ALASKAN NATIVE: A person having origins in any of the original peoples of North America and who maintains cultural identification through tribal affiliation or community recognition.

ASIAN: A person having origins in any of the original peoples of East Asia, Southeast Asia or the Indian subcontinent. This area includes, for example, China, India, Indonesia, Japan, Korea and Vietnam.

BLACK, NOT OF HISPANIC ORIGIN: A person having origins in any of the black racial groups of Africa.

HISPANIC: A person of Mexican, Puerto Rican, Cuban, Central or South American or other Spanish culture or origin, regardless of race.

PACIFIC ISLANDER: A person having origins in any of the original peoples of Hawaii; the U.S. Pacific territories of Guam, American Samoa, and the Northern Marinas; the U.S. Trust Territory of Palau; the islands of Micronesia and Melanesia; or the Philippines.

WHITE, NOT OF HISPANIC ORIGIN: A person having origins in any of the original peoples of Europe, North Africa, or the Middle East.